CHEMICAL CHANGES INDUCED BY STARCH AND STARCH PRODUCTS IN ACRYLONITRILE AND STYRENE

by

JOSEPH ROSENBERG

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INTRODUCTION

"No substance has been investigated more and is still less known." This observation on starch in 1836 by J. C. Poggendorff in "Annalen der Physik" was still found to be appropriate by Sponsler (27) in 1922. Today the statement would be no less true, for the structures of the starch molecule and granule are, at best, highly controversial.

Starch comes to man as one of the most abundant bounties of nature. As a result, man seeks to utilize the material to its fullest possible extent. In its natural form, starch has a large variety of uses. These are extended immeasurably by the potential possibilities created as more and more of its chemical derivatives are prepared. Many of these uses owe their existence to the complexity of starch, and yet it is this very complexity which may limit its utilization.

The enigmatic structure of starch and its behavior under various conditions has led to the formulation of many hypotheses which conflict and even refute each other. This investigation was undertaken as a consequence of the evaluation of certain results, which will be mentioned below, obtained both by this laboratory and others. It is intended to show that numerous seemingly anomalous results could well be attributed to the existence of a free radical structure in starch. This will be attempted by the utilization of starch as a catalyst in the polymerization and decomposition of acrylonitrile and

in the polymerization of styrene.

LITERATURE REVIEW

In the evaluation of starch, its alkali lability is often taken as an indication of its source and past treatment and of its desirability for various uses. In the consumption of alkali by starch, it is generally considered that aldehydic end groups are the focal points for attack by alkali. This explanation does not entirely answer the many questions raised by the alkali consumption of starch and by the phenomena that are associated with it.

The reducing power of carbohydrates was first explained by Nef who believed that the equilibrium shown in Fig. 1 existed in alkaline solution. This concept is generally accepted today. The enediols of glucose are believed to split at the double bonds giving rise to radicals containing divalent carbon. For example, the 1, 2 enediol would produce the components shown in Fig. 2. The great reactivity of the divalent carbon would enable it to absorb oxygen quite readily, yielding formic acid from the hydroxy methylene and d-arabonic acid together with d-ribonic acid from the methylene enol of arabinose.

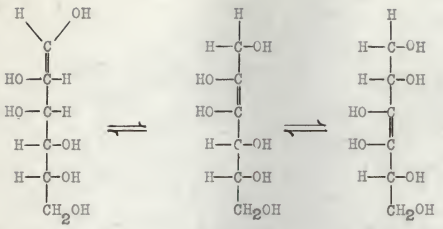
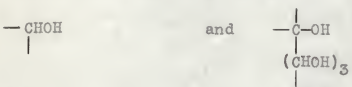


Fig. 1. Enediol equilibrium of glucose in alkaline solution.

Evans and his school have investigated the enediol hypothesis quite thoroughly. They have found no evidence to the contrary, as far as simple sugars are concerned. Rather, they have amassed a great amount of information regarding the equilibrium of the enediol formation under various conditions, not only for glucose, but for many other sugars. Thus, Evans, Edgar and Hoff (11) offer proof that the equilibrium is a function of the alkali concentration and of the temperature.



hydroxy methylene methylene enol of arabinose

Fig. 2. Products of enediol splitting.

If this enediolic formation is used in explaining the alkali lability of starch it falls far short of accounting for

the amount of alkali consumed, unless it is accompanied by glucosidic scission, occurring at the same rate. The starch molecule is considered to have a molecular weight of approximately 300,000 and to terminate in one aldehydic end group. A simple calculation would show that the alkali number of a given starch, which represents the amount of alkali consumed by one gram of it in one hour, is very large in comparison to the amount of alkali that could be consumed by one aldehyde group per molecular weight of 300,000.

To explain this, Taylor (29) postulated that the alkaline decomposition of starch proceeds from an initial attack of the terminal aldehyde group, which is followed by a progressive destruction of the glucose residues.

Although the concept of glucosidic scission could also explain the large consumption of alkali by starch, it was shown to be very unlikely by the work of Evans and Benoy (10). In their experiments with the alkaline oxidation of maltose they found that of the two kinds of decomposition open to the maltose molecule, enediolic splitting is rapid while hydrolysis is very slow. As further evidence against this theory, Lewis and Buckborough (17), in treating glucose and maltose with alkaline peroxide, found that the ratio and nature of the oxidation products obtained by using the two sugars, differed greatly. This variation was attributed to the stable presence of the glucosidic linkage.

Taylor and Keresztesy (30) increased the alkali lability of starch by ball-milling it. In an attempt to explain this increase, their contention was that, in addition to producing more aldehydic end groups by disrupting chains at the glucosidic linkages, the existing end groups were made more available. They believed that hydrogen bonding produced bundles of chains which were also dovetailed together with other chains. This shielded aldehyde groups which would otherwise be chemically free. By subjecting starch to various treatments, as in ball-milling, the aldehydic end groups were uncovered and made more available.

If the hypothesis of Taylor and Keresztesy (30) were correct, it would be logical to assume that the more available water is to a given starch the higher is its alkali lability. The opposite was shown to be true by Barham and Wagoner (6) in a study of the effects of cure on sweet potato starches. When starch was solvent extracted a reduced rate of availability of water for swelling was accompanied by increased alkali lability. Their results indicated that some kind of structural change was caused by solvent extraction. It would seem that by not being able to readily pass through the starch chains, the alkali structurally upsets the existing configuration to the extent that an alkali consuming component is created in starch.

A return to the field of sugars produces a concept which finds some support in the literature and is favorable from the

standpoint of starch chemistry. Levene (16), in seeking to account for the activity of glucose, also made use of a free radical theory. He explained the results obtained by various workers in the fields of biology and chemistry by assuming the existence of an "active glucose", to which he attributed a free radical structure, obtained from the severing of the oxygen bridge of the lactal forms of glucose, as shown in Fig. 3.

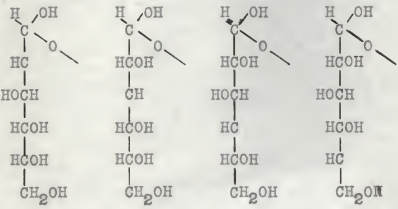


Fig. 3. Lactal forms of glucose with severed oxygen bridges.

Among other results, Levene (16) quoted Euler and co-workers as finding that glycogen ferments at a higher rate than free glucose. This fact is made even more significant when the high rate of dissociation by animal tissues is considered. Practically all those working on the subject have come to the conclusion that glucose is in a more labile form in glycogen than in ordinary glucose. Levene stated that in a given process, the reaction was dependent on the maintenance of the proper conditions conducive to the existence of one of the forms shown in Fig. 3.

Examining the literature in the light of this theory leads one to view it favorably. Clifton and Ort (8) found that solutions of glucose contained a small but definite amount of a very powerful reductant which exists in dynamic equilibrium with the main bulk of ordinary glucose. They calculated the concentration of active glucose as 1 part in 266,000, and postulated that, due to strain in the glucose molecule, the lactal ring might be broken with the formation of a free radical. Roepke and Ort (23) studied the rate of formation of active glucose as a function of temperature and hydrogen-ion concentration. Their results showed that at pH 13 the rate is 1,780,000 times greater than at pH 7.4. At 100° C. the rate is about 24,000,000 times faster than at 18° C.

The idea of a strain existing in the highly complex starch granule, with the subsequent formation of free radicals, is even easier to accept. Thus, Barham and Campbell (2) explained their results on this basis. Whenever they removed the lipids from starch granules, they obtained an increase in alkali lability, which led to the view that the removal of these substances may have permitted the formation of more inter and intramolecular hydrogen bondings which caused the chains to assume positions of still greater strain than exist in a starch granule which is already under a similar but smaller strain.

In the chlorination of starch by liquid chlorine, Barham and Thomson (5) reported a black induction product which

possessed properties characteristic of free radicals, according to the thesis of Thomson (31). This could be a condition in which the incidence of active glucose residues is very high, resulting from the effect of hydrogen chloride on the lactal interconversion.

Thomson (31), in his thesis on the direct chlorination of starch, postulated a mechanism involving the presence of a free radical in starch. The dichloride was reported as having colors which ranged from orange-red to blue, but which faded soon after it had been removed from the autoclave. A tetrachloride product gave a reversible color change between yellow and blue, depending on whether water or benzene was added to the product. All of these suggest free radicals. Barham and Thomson (5), in an unpublished report, proposed that the liquid phase chlorination of starch may have been initiated by an active center of the starch itself, as shown by Fig. 4.

$$R\cdot + Cl_2 \longrightarrow R\text{-}Cl + Cl\cdot$$

Fig. 4. Postulated free radical reaction of starch with chlorine.

Barham, Stickley and Thomson (3) successfully carried out the addition of chlorine to benzene without the presence of light, but in the presence of starch and its chlorine derivatives. They regarded this as evidence of the existence of a free radical within the starch structure. The fact that the black induction product catalyzed the addition reaction more effectively than starch itself, agrees with the belief expressed

above that a higher incidence of active glucose residues may exist in the induction product which could possibly account for its high absorption of light.

Much work has been published on the polymerization of unsaturates in the presence of free radicals. Noteworthy among these are the papers of Taylor and Jones (28), Cramer (9), and Rice and Sickman (22). Each of them showed that only with the aid of a free radical-producing substance would olefins polymerize.

Many workers have shown that in initiating a chain, the free radical of the catalyst becomes one of the ends of the polymer chain. Pfann, Solley, and Mark (19) did this by treating styrene with p-bromobenzoyl peroxide and determining the bromine content of the polymer. Pfann, Williams, and Mark (20) pointed out the generally accepted free radical chain mechanism of the polymerization of vinyl derivatives. This was in agreement with the conclusions of Breitenbach and Taglieber (7).

The decomposition of organic compounds below their normal decomposition temperature in the presence of free radicals is widely accepted. Rice and Herzfeld (21), Sickman and Allen (26), and Frey (12) have shown the free radicals to be necessary to this decomposition.

Kern and Fernow (14) have experimented extensively with the polymerization of acrylonitrile by benzoyl peroxide. They found that even at 160° C. no polymerization occurred unless

the catalyst was present. The acrylonitrile decomposed only in the presence of free radical producing substances. One of the decomposition products was identified as hydrogen cyanide; no other product could be found. As a result they postulated the reaction shown in Fig. 5.

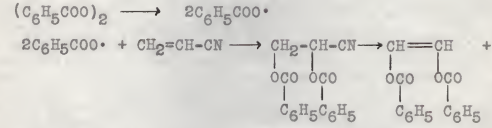


Fig. 5. Direct reaction of benzoyl peroxide free radical with acrylonitrile.

METHODS

Preparation of Starch Samples

For the final work of this investigation, 11 different samples of starch and starch products were prepared as described below.

No. 7. This was a commercial corn starch. It was used in its original form except for being placed in a vacuum desiccator which was evacuated and the displaced air replaced with dry nitrogen gas, a procedure repeated five times. In addition, the other samples were prepared from it and all were stored under nitrogen.

No. 7D. Sample 7 was dried for 15 hours in a vacuum oven at 105° C., followed by saturation with nitrogen.

No. 7X. Sample 7 was solvent extracted by refluxing it in 85 per cent methanol for five two-hour periods. The methanol was removed by washing with distilled water and the starch was thoroughly dried and pulverized. It was placed in a vacuum desiccator which was evacuated and then saturated with nitrogen.

No. 7DX. Sample 7X was dried in a vacuum oven for 15 hours at 105° C., and again saturated with nitrogen.

No. 7M. Sample was placed in a ball-mill equipped with a specially constructed lid which allowed it to be evacuated and saturated with nitrogen. Thus, the milling proceded under an atmosphere of nitrogen for 336 hours. It was transferred to a jar for storage without coming in contact with oxygen. This operation was performed in a sealed cabinet through which nitrogen passed under pressure, but which permitted both the insertion of the worker's hands and observation of the manipulations.

No. 7MX. To obtain this sample, sample 7X was ball-milled by the same method used on sample 7 to obtain sample 7M.

No. 7DM. Sample 7D was ball-milled by the same procedure used in obtaining sample 7M.

No. 7DMX. Sample 7DX was ball-milled to produce this product by the above method.

Hydrogen Chloride-Treated Starch. Sample 7DX was treated in the following manner, as described in the thesis of Thomson (30). It was placed in a tube fitted with a sintered glass bottom through which dry hydrogen chloride was passed for eight and one-half hours at 70° C. The sample was then placed under a vacuum followed by the sweeping of nitrogen through it for 15 hours. A dry, black, powdery product was obtained.

Induction Product (IP). This product was prepared as described in the paper by Barham and Thomson (4) on the chlorination of starch by liquid chlorine. The product was removed from the autoclave and then pyrolyzed at 70° C. and 15 mm for 48 hours, followed by saturation with nitrogen.

Starch Chloride (CA4). This product was prepared according to the method of Barham and Thomson (4) and pyrolyzed for 48 hours at 70° C. and 15 mm, followed by saturation with nitrogen gas. Analysis showed its structure to approach the dichloride of starch.

All samples of starches and starch products were transferred from their containers in the cabinet mentioned above. Dry nitrogen gas flowed constantly through the cabinet in which phosphorus pentoxide was used to keep the atmosphere dry.

Other Materials Used

Acrylonitrile. The Eastman, practical product was dried over anhydrous calcium sulfate and distilled. The fraction

distilling at 76.5° to 77.5° C. was used.

Styrene. The Eastman, practical product was distilled through a packed column at 40° C. and 10 mm, immediately before use. Tests for polystyrene gave negative results.

Polymerization and Decomposition of Acrylonitrile

These experiments were carried out in pyrex glass tubes, measuring 35 by 150 mm. Each tube had a ground glass, 19/38, standard taper joint into which was fitted an adapter which had a 24/40 standard taper female joint at the opposite end. Midway between the two joints, connection was made between a capillary tube on the inside of the adapter, which extended down to within a few mm of the bottom of the reaction tube, and a short piece of glass tubing on the outside of the adapter which eventually connected to a source of nitrogen gas. A Liebig reflux condenser was placed in the 24/40 joint. Any acrylonitrile vapors that succeeded in escaping the condenser were caught by a tared ice-trap connected to the top of the condenser.

A starch sample of about 5 grams, weighed on a dry basis, and a weighed amount of acrylonitrile were placed in a tared tube and the apparatus assembled. The mixture was allowed to reflux in a water bath at 80° C. for 24 hours, with dry nitrogen gas continuously passing through it and providing both an inert atmosphere and agitation. At the end of that

period the tube and its contents were cooled and then weighed, and any increase in weight of the ice-trap added to this value. The difference between the weights taken before refluxing and after constituted the loss of acrylonitrile. The tube was placed in a vacuum desiccator, at room temperature, to remove the excess acrylonitrile, after which it was placed in a vacuum oven at 105° C. (or at 70° C., for the experiments in which the chlorinated starches were used) for 15 hours. The tube was then cooled and weighed and the increase in weight was calculated by subtracting the initial weight of starch from this final weight. Kjeldahl analyses were made on all the products.

Polymerization of Styrene

Weighed samples of about five grams of starch were placed in tared glass stoppered containers of about 75 ml capacity, originally designed as centrifuge tubes, and 10 ml of styrene added. Then the tubes were evacuated and saturated with nitrogen five times, and sealed. They were placed in a water bath equipped with a shaker and maintained at 35° C. At the end of three hours, the tubes were removed and the excess styrene evaporated at 45° C. and 13 mm. The tubes were then placed in a vacuum oven at 105° C. (or 70° C. for chlorinated starches) for 15 hours. After being cooled, they were weighed again to obtain the increase in weight resulting from the

reaction.

The product was removed from the tube with the aid of 100 ml of benzene and agitated in a Waring Blendor for one hour. The mixture was filtered and the clear liquid poured into 250 ml of methanol. The resultant precipitate of polystyrene was weighed by filtering the mixture through a sintered porcelain crucible which was then dried at 65° C. and cooled.

Alkali Labilities

The alkali labilities of the various starches were determined by a modification of the method of Schoch and Jensen (24) which gives greater precision than the unmodified method, as mentioned by Barham and Campbell (2).

DISCUSSION OF RESULTS

Table 1 contains the values obtained for the alkali labilities of the starches used. An explanation of the procedure followed in obtaining these starch products was given on page 10. Although the alkali number is actually a rate, it is expressed in ml of 0.1 N alkali per gram of starch. The significance of the results shown in Table 1 will be discussed in relation to the data presented on the following pages.

Table 1. Alkali lability.

Sample of starch:	Alkali number in ml of 0.1 N NaOH per g of starch
7	8.42
7D	8.99
7X	9.79
7M	9.63
7DX	10.05
7DM	10.51
7MX	10.27
7DMX	9.87

Decomposition of Acrylonitrile

The values obtained for the decomposition of acrylonitrile are shown in Table 2. They were calculated by dividing the loss in weight of the refluxing material by the product of both the initial weight of acrylonitrile and the weight of starch used, and multiplying this by 100. Thus, the value shown represents the per cent decomposition of acrylonitrile per gram of starch used.

Table 2. Decomposition of acrylonitrile.

Sample of starch or of starch derivative:	Experiment I	Experiment II	Average in per cent decomposition per g of starch
7	1.18	1.32	1.25
7D	2.65	1.76	2.21
7X	2.69	2.86	2.78
7M	1.36	0.90	1.13
7DX	2.28	1.90	2.09
7DM	4.40	3.05	3.73
7MX	3.12	3.46	3.29
7DMX	1.57	1.33	1.45
Hcl	0.84	0.39	0.62
IP	1.98	0.57	1.28
CA4	0.85	0.95	0.90

A blank was run which showed a loss which was much smaller than any found in those experiments which were performed with the use of starch and was probably caused by a very slight amount of material remaining on the condenser walls. As mentioned above, many workers (12, 21, 26) have shown that a free radical must be present to enable a substance to decompose below its normal decomposition temperature. During the process, the decomposing substance is split into free radicals. Kern and Fernow (14) have shown that benzoyl peroxide, a free radical producing substance, must be present if this decomposition is to occur in acrylonitrile. They ascertained that the gas evolved was hydrogen cyanide, but could identify no other products. This led them to suggest that the remainder of the molecule, a free radical, formed a compound with the free radicals of benzoyl peroxide, as shown on page 10. Possible evidence for the latter process occurring in starch will be presented later. In addition, tests performed in the present work on the escaping gas showed only the presence of hydrogen cyanide, in agreement with the data of Kern and Fernow.

It was believed that the various treatments accorded the natural starch might have an effect on any strains existing in the granule, thus affecting possible free radical structure. In order to observe the relation between any alteration of the activity of these free radicals in the consumption of alkali and in the decomposition of acrylonitrile, the following

procedure of graphing was used. An arbitrary number was assigned to each treatment used on the starch and where several treatments were used, they were added together to give the values shown in Table 4. They were not intended to indicate the relative effect of the various procedures and were merely used as a method of presentation. Table 3 lists the numbers given to each procedure. When these numbers were added together in the right combination, the value assigned to each starch sample, as shown in Table 4, was obtained. For example, sample 7DX which was corn starch (1) that had been solvent extracted (5) and then vacuum dried (3) had the value nine (1+5+3). The values of Table 4 were used for the abscissas of the graphs of this thesis.

Table 3. Numbers assigned to each treatment of starch.

Treatment	Number
Natural starch	1
Vacuum dried at 105° C.	3
Solvent extracted	5
Ball-milled	7

Table 4. Abscissa value assigned to each starch sample for the purpose of graphing.

Starch sample	:	Value
7		1
7D		4
7X		6
7M		8
7DX		9
7DM		11
7MX		13
7DMX		16

In Fig. 6, both the alkali number and per cent decomposition of acrylonitrile were plotted against these arbitrary units. Although no quantitative relationship exists between the two curves, it may be noted that a qualitative parallelism exists. Thus, increases and decreases in the alkali lability curve are accompanied by increases and decreases in the decomposition curve that tend to parallel those of the first curve. This would appear to indicate that a given modification of granular structure affects decomposition of acrylonitrile and alkali consumption of the starch in a similar manner. If decomposition of acrylonitrile is accepted as occurring through the agency of free radicals in starch, then it would appear likely that alkali lability is, at least to a certain extent, a function of the same reactant, namely, the free radicals of starch.

Consideration of the decomposition values in Table 2 show that those values obtained with the use of chlorinated

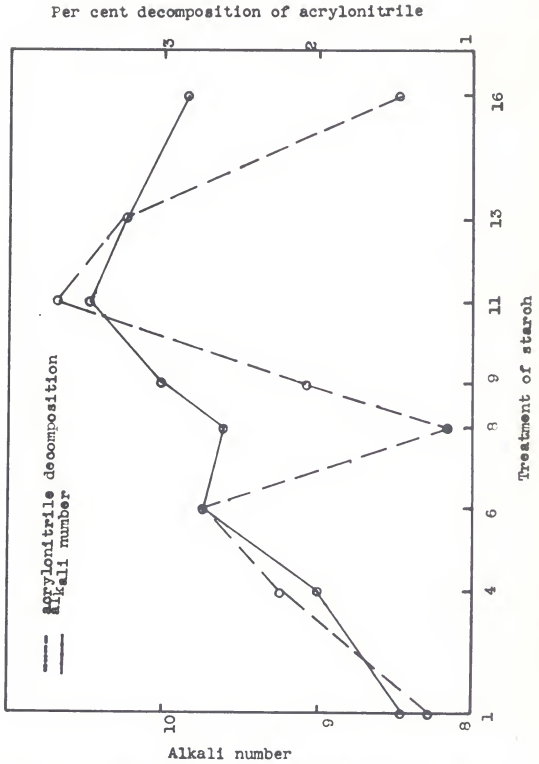


Fig. 6. A comparison of alkali number and per cent decomposition of acrylonitrile.

products are rather low. It is suggested that either steric influences or those of polarity retard contact between the non-polar acrylonitrile and the postulated active centers. Of great interest is the fact that of the three products, the induction product has the highest value which would appear to be in agreement with the above mentioned unpublished hypothesis of Barham and Thomson (5) that the incidence of active glucose residues is relatively high in the black induction product.

Polymerization of Acrylonitrile

Table 5 contains the results of the polymerizations of acrylonitrile induced by the various starch samples. Two average polymerization values are given for each experiment. One was obtained by dividing the increase in weight, observed after drying the final product, by the initial weight of starch and then multiplying by 100. The other value was obtained by means of a Kjeldahl analysis for nitrogen. Per cent nitrogen of the sample was divided by 0.2640, the per cent nitrogen of polyacrylonitrile, thereby giving the per cent polyacrylonitrile of the product.

A blank showed no measurable extent of polymerization of acrylonitrile, while the probability of a starch free radical was supported by positive polymerization results. If the polymerization data of Table 5 are plotted on the same

Table 5. Polymerization of acrylonitrile.

Starch sample	Per cent polymerization by increase in weight			Per cent polymerization by nitrogen analysis		
	I	II	average	I	II	average
7	*	1.79	1.79	1.78	1.81	1.80
7D	2.07	1.99	2.03	1.51	1.47	1.49
7X	2.82	2.36	2.59	2.19	1.81	2.00
7M	1.97	1.67	1.82	1.85	1.66	1.76
7DX	*	1.36	1.36	1.36	1.39	1.38
7DM	1.06	1.08	1.07	0.87	0.83	0.85
7MX	1.52	1.55	1.54	1.51	1.28	1.40
7DMX	0.65	1.06	0.86	0.41	1.06	0.74
HCl	2.59	3.56	3.08	3.03	3.37	3.20
IP	decrease in weight			0.56	0.53	0.55
CA4	2.16	2.07	2.12	4.77	4.77	4.77

* Value rejected due to obvious experimental error.

coordinates as alkali-lability, a poor parallel trend between the two curves, with respect to the various treatments, is to be observed. Figure 7, using polymerization values obtained from nitrogen analysis, shows that the parallelism exists. Polymerization by increase in weight will produce the same type of graph showing correlation with alkali lability. The explanation of the relatively poor correlation apparently lies in the decomposition process of acrylonitrile. Since it was shown above that the decomposition of acrylonitrile proceeds through a free radical mechanism, it may be postulated that the reaction mixture consisted of acrylonitrile, its free radical decomposition product, hydrogen cyanide and starch. Competition obviously existed between the acrylonitrile and the vinyl free radical for reaction with the active centers of starch, with the result that polymerization did not proceed as

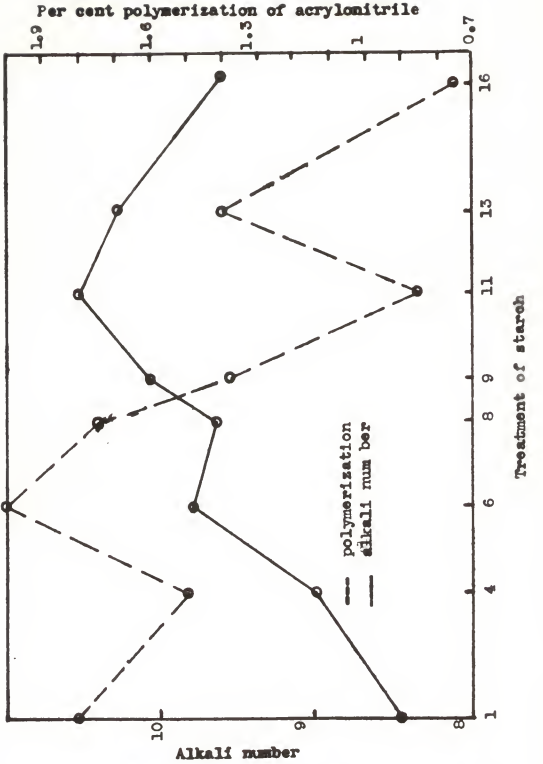


Fig. 7. A comparison of alkali number and per cent polymerization of acrylonitrile.

uniformly as it would have if only acrylonitrile and starch were present. Since this decomposition did not occur in styrene, a better correlation was obtained between its polymerization trends and alkali lability.

Consideration of the results of Table 5 will show them to support this hypothesis. Where the polymerization values by increase in weight differ from the values obtained by nitrogen analysis, the tendency is for the former values to be slightly higher. That is the expected result if a free radical decomposition of acrylonitrile occurred. In the process, the vinyl free radicals react with the free radicals of the starch or with any activated polymer chains, resulting in a chain termination step, as suggested in Fig. 8, where R· represents the starch free radical.

$$H_2C{=}C{-}CN \longrightarrow \dot{H}C{=}\dot{C}H + HCN$$

$$2R\cdot + \dot{H}C{=}\dot{C}H \longrightarrow \begin{matrix} R & R \\ | & | \\ HC{=}CH \end{matrix}$$

Fig. 8. Postulated reaction between vinyl free radicals and starch free radicals.

Thus, while this reaction could be detected by an increase in weight of the product, no increase in its nitrogen content would occur. This would make the per cent polymerization, calculated by nitrogen content, slightly lower than the value calculated from increase in weight. The results obtained appear to support this theory.

Consideration of the acrylonitrile polymerization values acquired with chlorinated products shows that direct reactions probably occurred between the olefin and the starch product. Thus, while a decrease in weight was experienced by the induction product, it showed a gain of nitrogen content. The starch chloride gave an increase in weight but its polymerization value, as calculated by nitrogen content, was 225 per cent higher. Support by the literature of a direct reaction will be discussed below in relation to styrene. The hydrogen chloride-treated starch showed an increase in weight that corresponded fairly well to its nitrogen content, indicating polymerization, induced by free radicals.

Polymerization of Styrene

The results obtained in the polymerization of styrene are listed in Table 6. Per cent polymerization by weight was calculated by dividing the increase in weight of the final dried product by the initial weight of starch and then multiplying by 100. Per cent polymerization by extraction was calculated by dividing the weight of polystyrene extracted by the method described on page 15 by the initial weight of starch and then multiplying by 100.

A blank experiment containing no starch was performed and showed no polymerization. It may be observed that the polymerization values obtained by increase in weight and those

obtained by extraction differ. This may be due to the fact that low polymers of styrene like dimers are soluble in methanol (18). Since the extraction procedure depended upon

Table 6. Polymerization of styrene.

Starch sample	Per cent polymerization by weight			Per cent polymerization by extraction		
	I	II	average	I	II	average
7	0.86	0.56	0.71	0.28	0.23	0.26
7D	0.36	0.18	0.27	0.23	0.25	0.24
7X	0.78	0.76	0.77	0.37	0.33	0.35
7M	0.38	0.20	0.29	0.36	0.20	0.28
7DX	0.82	0.74	0.78	0.41	0.43	0.42
7DM	2.35	1.98	2.17	1.68	0.86	1.08
7MX	0.14	0.12	0.13	0.33	0.19	0.26
7DMX	1.24	1.71	1.48	1.22	0.88	1.05
HCl	2.49	1.94	2.22	0.37	0.25	0.31
IP	5.34	6.85	6.10	3.57	5.57	4.57
CA4	20.05	20.10	20.08	10.59	9.80	10.20

precipitation of polystyrene in methanol, this deviation due to the solubility of extremely low polymers, would have occurred. Another possible explanation is that of an addition reaction between the starch and styrene that would be noted by an increase in weight but not by extraction and precipitation of polystyrene. Both or either of these hypotheses could account for the lower polymerization value obtained by extraction than that obtained by weight increase.

The results listed in Table 6 were plotted on the same coordinates as the alkali lability data. A fairly similar qualitative trend was indicated between alkali lability and polymerization of styrene for the various treatments of

natural starch as may be seen in Fig. 9. Thus, here too, it would seem that, at least to a certain degree, alkali lability and the observed polymerization of styrene are a function of the same reactant. The reactant or initiator in the case of styrene polymerization at low temperatures is a free radical, as experiences of this investigation and those of other workers, have indicated. Thus, starch free radicals would also appear to play an important role in alkali consumption.

The products obtained from polymerization of styrene with starch were interesting and polymerization was manifested mainly by the presence of hard substances which appeared to be soluble in benzene. Alone, of the natural starch products, sample 7D assumed a yellowish color. The black induction product seemed to become solidified. The chloride product was an impenetrable solid mass, soluble in benzene, and Table 6 shows that styrene was utilized by the substance quite extensively. Extraction gave a yield of about 50 per cent, suggesting some kind of direct reaction. Barham and Thomson (4) have postulated that the dichloride of starch is a 1, 2 diketone. Schonberg and Mustafa (25), in working with olefins and diketones, found that a reaction occurred between unsaturates, like styrene and stilbene, and 1, 2 diketones, like phenanthraquinone, to give a stable product. Figure 10 contains a postulated reaction between starch dichloride and styrene, based upon the illustration of Schonberg and Mustafa. Although a reaction occurred, it was not likely to be exactly

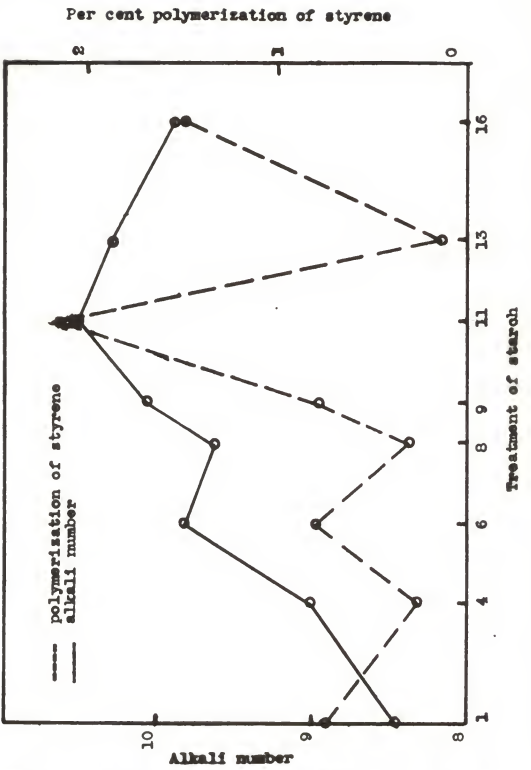


Fig. 9. A comparison of alkali number and per cent polymerization of styrene.

of this type because of the distorting presence of oxygen in the ring. Styrene consumed in a direct reaction would increase the weight but would probably not be included in the polystyrene extraction.

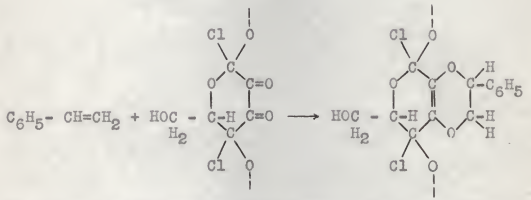


Fig. 10. Postulated reaction between starch dichloride and styrene.

Effect of Structural Modifications on Starch Activity

The results presented above, in addition to those found in the literature, suggest that various treatments of starch modify its structure in such a manner as to affect certain of its activities. Some of these activities, such as the initiation of the polymerization of unsaturates or the decomposition of organic substances, have definitely been attributed to free radicals in work not connected with starch. Another activity of starch, its alkali consumption, has been shown to be affected qualitatively similar to the manner in which the above accepted free radical activities were affected.

Together with much support from the literature, this could lead to the assumption that alkali consumption is at least partially induced by a free radical structure existing in starch.

Thus, each procedure such as solvent extraction, ball-milling, or vacuum drying must alter the granular structure in a definite way in order to enhance or diminish strains which would manifest themselves in increased or decreased free radical activity. Vacuum drying apparently rendered the granule in a condition that displayed a greater incidence of free radicals. Alkali lability, decomposition of acrylonitrile, and styrene polymerization, tended to increase after this treatment of the starch, alone and in combination with other treatments. An explanation may be found in Alsberg's (1) opinion that starch molecules are in a semi-crumpled condition in the granule, and dehydration causes them to contract while hydration impels them to extend. In their contracted condition, strain would be increased, a condition favorable to the creation of free radicals. Barham and Campbell (2) explain it by suggesting that when water is removed from the granule, the hydrogen bonds, that part of the water formed with the molecules, are broken, permitting the formation of new and stronger hydrogen bonds which would be conducive to strain as a result of the more closely packed condition.

Solvent extraction, as always, resulted in an increase of alkali lability. Acrylonitrile decomposition and styrene

polymerization also tended to be enhanced. Thus, it would seem that an increase in hydrogen bonding, produced by the removal of lipids, resulted in a magnification of the free radical effect due to increased strain. The data of Barham and Campbell (2), and Barham and Wagoner (6) apparently agree with this hypothesis, in that solvent extraction was followed by an increase in alkali consumption. Barham and Campbell account for increased alkali consumption upon solvent extraction by postulating that with the removal of lipids, which probably are associated with the starch chains through hydrogen bonding, intra and intermolecular hydrogen bonding are increased, resulting in more strain. Here, too, the acrylonitrile polymerization results, although indicative of free radicals, are not as well correlated with alkali lability as the other results. The significance of this will be discussed below.

The ball-milling of starch produced a condition of increased alkali lability and tended to increase its activity with respect to acrylonitrile decomposition and styrene polymerization, pointing to a possibly higher concentration of free radicals. There is much reference in the literature to this enhanced activity. As pointed out above, Taylor and Keresztesy (30) found increased alkali lability. Lampitt, Fuller, and Goldenberg (15), in an extensive series of papers, report among other data the increased reducing power of ball-milled starch with the use of a wide variety of oxidants.

These authors, in addition to others such as Sponsler (27) and Hess and Steurer (13), found that the X-ray diffraction pattern of starch diminished greatly when it was ball-milled. In an attempt at explanation of this, Hess and Steurer significantly mentioned the effect on granular structure that must occur from the "crushing-strain" of the ball-mill. Thus, it would seem that during this destructive procedure free radicals could be produced.

With ball-milling, the activity of the starch again tended to be increased in all experiments except in acrylonitrile polymerization. As was postulated above, this would seem to result from the competition that existed between the vinyl free radicals and the acrylonitrile for the starch active centers and the activated growing polymer chains. Reactions between the vinyl free radical and the active centers would constitute a chain termination step which would disrupt the polymerization process and account for the marked disagreement of acrylonitrile polymerization results with the other data.

SUMMARY

1. Characteristics that are usually attributed to free radical behavior were observed in starch. These properties were the ability to induce polymerization of acrylonitrile and styrene and the decomposition of acrylonitrile.

2. Upon treatment of starch with such procedures as vacuum-drying, solvent extraction, and ball-milling, a qualitative correlation was noted between trends in the aforementioned activities of starch and its alkali lability. This indicated that, at least to a certain extent, they are functions of the same component of starch. This component appeared to be related to the degree of strain existing in the granule.

3. Products of starch, namely, hydrogen chloride-treated starch, the induction product of the liquid phase chlorination reaction, and chlorinated starch, possessed the same ability to induce polymerization of acrylonitrile and styrene, as well as decomposition of acrylonitrile. In addition, a reaction was seen to occur between starch dichloride and styrene.

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LITERATURE CITED

(1) Alsberg, C. L.
Structure of the starch granule. Plant Physiol., 13: 295-330. 1938.

(2) Barham, H. N., and C. L. Campbell.
Unpublished data from this laboratory.

(3) Barham, H. N., E. S. Stickley, and T. R. Thomson.
Unpublished data from this laboratory.

(4) Barham, H. N., and T. R. Thomson.
The chlorination of starch in anhydrous liquid chlorine at 70° C. The mono-, di-, and trichlorides of starch. Amer. Chem. Soc. Jour., 70: 3321-3326. 1948.

(5) Barham, H. N., and T. R. Thomson.
Unpublished data from this laboratory.

(6) Barham, H. N., and J. A. Wagoner.
Effect of time and conditions of cure on the carbohydrate composition of sweet potatoes and the properties of their starches. Jour. Agr. Res. 73: 255-280. 1946.

(7) Breitenbach, J. W., and V. Taglieber.
Polymerization of vinyl derivatives in the presence of benzoyl peroxide. Deut. Chem. Gesell. Ber. 76B: 272-280. 1943.

(8) Clifton, C. E., and J. M. Ort.
Active glucose. Jour. Phys. Chem. 34: 855-862. 1930.

(9) Cramer, P. L.
The decomposition of tetraethyllead in ethylene. Amer. Chem. Soc. Jour. 56: 1234-1237. 1934.

(10) Evans, W. L., and M. P. Benoy.
The mechanism of carbohydrate oxidation. XI. Action of potassium hydroxide on maltose. Amer. Chem. Soc. Jour. 52: 294-307. 1930.

(11) Evans, W. L., R. H. Edgar, and G. P. Hoff.
The mechanism of carbohydrate oxidation. IV. The action of potassium hydroxide on d-glucose and d-galactose. Amer. Chem. Soc. Jour. 48: 2665-2677. 1926.

(12) Frey, F. E.
Pyrolysis of saturated hydrocarbons. Indus. and Engin. Chem. 26: 198-203. 1934.

(13) Hess, K., and E. Steurer.
Thermal or mechanical chemical reactions of ball-milled high polymers. Ztschr. Physik. Chem. 193: 234-257. 1944.

(14) Kern, W., and H. Fernow.
Polymerization of acrylonitrile and polyacrylonitrile. Jour. prakt. Chem. 160: 281-295. 1942.

(15) Lampitt, L. H., H. C. Fuller, and N. Goldenberg.
The fractionation of wheat starch. Jour. Soc. Chem. Indus. 60: 1-6, 25-29, 69-72, 99-111. 1941.

(16) Levene, P. A.
Active glucose. Chem. Rev. 5: 1-16. 1928.

(17) Lewis, W. L., and S. A. Buckborough.
The structure of maltose and its oxidation products with alkaline peroxide of hydrogen. Amer. Chem. Soc. Jour. 36: 2385-2397. 1914.

(18) McGovern, J. J., J. M. Grim, and W. C. Teach.
Determination of monomer in polystyrene. Anal. Chem. 20: 312-314. 1948.

(19) Pfann, H. F., D. J. Solley, and H. Mark.
Mechanism of peroxide initiated styrene polymerization. Amer. Chem. Soc. Jour. 66: 983-985. 1944.

(20) Pfann, H. F., V. Z. Williams, and H. Mark.
Mechanism of peroxide initiated styrene polymerization. Jour. Polymer Research. 1: 14-21. 1946.

(21) Rice, F. O., and K. F. Herzfeld.
The thermal decomposition of organic compounds from the standpoint of free radicals. Amer. Chem. Soc. Jour. 56: 284-291. 1934.

(22) Rice, O. K., and D. V. Sickman.
Polymerization of ethylene induced by methyl radicals. Amer. Chem. Soc. Jour. 57: 1384-1385. 1935.

(23) Roepke, M. H., and J. M. Ort.
The rates of formation of the active reductants of several sugars. Jour. Phys. Chem. 35: 3596-3611. 1931.

(24) Schoch, T. J., and C. C. Jensen.
A simplified alkali-lability determination for starch products. Indus. and Engin. Chem., Analyt. Ed. 12: 531-532. 1940.

(25) Schonberg, A., and A. Mustafa.
Reactions of ethylenes with 1, 2 diketones in the sunlight. Nature: (London). 153: 195. 1944.

(26) Sickman, D. V., and A. O. Allen.
Chains in the acetaldehyde decomposition. Amer. Chem. Soc. Jour. 56: 1251. 1934.

(27) Sponsler, O. L.
The structure of the starch grain. Amer. Jour. Bot. 9: 471-482. 1922.

(28) Taylor, H. S., and W. H. Jones.
The thermal decomposition of metal alkyls in hydrogen-ethylene mixtures. Amer. Chem. Soc. Jour. 52: 1111-1116. 1930.

(29) Taylor, T. C., H. H. Fletcher, and M. H. Adams.
Determination of the alkali-labile value of starches and starch products. Indus. and Engin. Chem., Analyt. Ed. 7: 321-324. 1935.

(30) Taylor, T. C., and J. C. Keresztesy.
Granule disintegration of cornstarch. Indus. and Engin. Chem. 28: 502-505. 1936.

(31) Thomson, T. R.
The direct chlorination of starch. Unpublished Doctor's thesis. Kans. State Col. Agr. and Appl. Sci. 174 p. 1945.

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